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Kinetic and thermodynamic equilibrium of asphaltenes sorption onto nanoparticles of nickel oxide supported on nanoparticulated alumina

Camilo Franco [a], Edgar Patiño [b], Pedro Benjumea [a], Marco A. Ruiz [a], Farid B. Cortés [a,*]

[a] Grupo de investigación Yacimientos de Hidrocarburos, Facultad de Minas, Universidad Nacional de Colombia, sede Medellín, Colombia
[b] Petroingeniería Regional de Antioquia, Petroraza S.A.S., Calle 80 Sur N° 47D 88, Sabaneta, Colombia

HIGHLIGHTS

- Nanoparticles of nickel oxide supported on a nanoparticulated matrix of alumina (SHS) were prepared.
- Adsorption affinity increased with increasing the NiO content on the alumina surface.
- Alumina-SHS nanomaterials can be used as excellent adsorbents for light and heavy oil upgrading.
- Complete asphaltenes sorption on Alumina-SHS can be achieved rapidly around 2 min.
- The asphaltenes sorption processes were analyzed in terms of isotherm, kinetics, and thermodynamics models.

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ABSTRACT

Nanoparticles can be used as adsorbents and catalyst in oil industry for *in situ* upgrading in the oil industry. The main objective of this study was to investigate the kinetic and thermodynamic equilibrium of asphaltene sorption onto nanoparticles of nickel oxide supported on nanoparticulated alumina at different temperatures, times, and concentrations. Alumina-supported nanoparticles were characterized by N_2 adsorption at −196 °C and X-ray diffraction. Complete asphaltene sorption on nanoparticles of nickel oxide supported on nanoparticulated alumina can be effectively reached at relatively short times (around 2 min), making this sorbent a good candidate for asphaltene sorption. The sorption equilibrium of asphaltene for alumina and alumina-supported nanoparticles at different temperatures (25, 40, 55, and 70 °C) over a wide range of asphaltene concentration, from 150 to 2000 mg/L, was determined using a static method. The Langmuir and Freundlich models were used for correlating the experimental data of the sorption equilibrium at different temperatures. Regarding to the Al and AlNi5 samples, the experimental data on asphaltene sorption isotherms were adequately adjusted by the Freundlich model. On the other hand, for the AlNi15 sample the experimental data were adequately fitted by the Langmuir model. The adsorption of asphaltene on NiO supported on alumina was much higher than that over alumina for the range of equilibrium concentrations tested. Pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data obtained at different concentrations of asphaltenes from 250 to 2000 mg/L for alumina and alumina-supported materials, with a better fitting to the pseudo-second-order model.

1. Introduction

Asphaltenes are defined as the fraction of a crude oil that is insoluble in low molecular weight paraffins such as *n*-heptane or *n*-pentane, while being soluble in light aromatic hydrocarbons such as toluene, pyridine, or benzene [1]. This definition based on solubility characteristics indicates a procedure to isolate asphaltenes from crude oils or bituminous materials, but it does not provide insight into their chemical structure. In fact, asphaltenes are not a chemical family per se, and may contain a large heterogeneity of chemical functionalities, which does not allow a complete definition of their molecular properties. However, it is widely accepted that the structure of asphaltenes is formed by polyaromatic cores attached to aliphatic chains and containing heteroatoms such as nitrogen, oxygen, sulfur, and metals such as vanadium, iron, and nickel [2]. Asphaltenes contain polar and non-polar groups (amphiphilic behavior) and tend to form colloidal aggregates. It has been reported that viscosity of heavy oils can dramatically increase by the asphaltene aggregation phenomenon [3].

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* Corresponding author. Address: Kra 80 N. 65-223, M3-100A, Colombia. Tel.: +57 4 4255137; fax: +57 4 2341002.
E-mail address: fbcortes@unal.edu.co (F.B. Cortés).

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The stability of asphaltenes in a crude oil depends upon a variety of factors rather than solely upon the asphaltene content of the oil. It has been pointed that high asphaltene content of oil is not necessarily associated with high risk of asphaltene precipitation; on the contrary, relatively light oils with low asphaltene content are more prone to undergo asphaltene precipitation and deposition, especially in sub-saturated oil reservoirs that are at pressures above bubble point [4].

Asphaltene deposition is a widely identified problem that occurs during production operations in the petroleum industry and generates large cost increase due to the necessity of prevention and removal of deposits. The precipitated and subsequently deposited asphaltenes can affect reservoir productivity, and cause plugging of pipes and processing equipment. Asphaltenes are also known to facilitate the formation of stable water-in-oil emulsions and to contribute to the poisoning of catalysts in petroleum refining processes [5,6].

After precipitation, asphaltenes can be adsorbed on rock surfaces inducing formation damage by reducing rock absolute permeability, oil relative permeability, and altering rock wettability. Aiming to understand process phenomenology and to find alternatives for avoiding productivity losses in oil reservoirs, several researchers have studied the adsorption of asphaltenes onto common mineral surfaces. Adsorption process is generally studied by extracting asphaltenes from oils and resolubilizing them in a model solvent [7]. Different mechanisms of surface layer formation have been identified depending upon the different nature of adsorbed asphaltenes, their concentrations, and the composition and morphology of the mineral surface. Both monolayer and multilayer adsorption have been reported. Regarding to monolayer adsorption, the most common physical model is the Langmuir model.

Gonzalez and Moreira [8] and Acevedo et al. [9] reported that the isotherms of asphaltene sorption onto mineral surfaces (quartz, calcite, clays) followed a Langmuir-type behavior, with a maximum adsorption capacity of 1–2 mg/m^2. Dubey and Waxman [10] performed adsorption experiments on a number of mineral surfaces and for a variety of solvents. They obtained Langmuir Type I isotherms for kaolin clay minerals with non-polar solvents and also with toluene solvent on common mineral surfaces. However, a Langmuir Type II isotherm was obtained for asphaltene adsorption from nitrobenzene solvent on kaolin. Piro et al. [11] studied asphaltene adsorption on rock under dynamic flow conditions and argued that, unlike static adsorption of asphaltene, in a dynamic flow regime asphaltene adsorption on rock is a continuous phenomenon which does not reach saturation. Pernyeszi et al. [12] studied the effect of different types of materials (quartz, bentonite, cliptonita, and two cores taken at different well depths) on the asphaltene adsorption process. Authors found that isotherms showed a type I behavior according to the IUPAC criteria. Rayes et al. [13] studied the adsorption of asphaltenes from light, medium, and heavy oils on reservoir rocks having different calcite and clay contents. Authors did not found significant differences in the adsorption of different asphaltenes. Depending on the mineralogical composition, the adsorbed amount varied between 18 and 45 mg/m^2. Higher asphaltene uptakes were reported as the clay content increased. Nassar et al. [7] investigated the effect of surface acidity and basicity of aluminas on asphaltene adsorption followed by air oxidation. Authors found that adsorption capacity was proportional to surface acidity. On the other hand, basic alumina showed the highest catalytic activity toward asphaltene oxidation.

A common characteristic of the above reported studies is that they aimed to evaluate the adsorptive properties of mineral powders or crushed rocks whose medium grain sizes are in the order of micrometers. Piro et al. [11] have suggested that a prevention method for avoiding asphaltene adsorption onto mineral surfaces would be to treat the rock with chemicals that have a higher tendency to adsorb on the rock in comparison with asphaltenes. This means a competition between fluids for mineral surfaces. Another alternative, in the line of using nanotechnology in improved oil recovery technologies, is to promote a competition between solid surfaces for asphaltenes. The idea is that nanomaterials with high adsorption capacity, due to its grain size, surface area, and mineral composition, are able to quickly capture asphaltenes from crude oils, improving oil mobility, and avoiding asphaltene aggregation and adsorption onto the rock surface.

In this line of research, the Alberta Ingenuity Centre for *In-situ* Energy at the University of Calgary is carrying out studies looking at *in situ* heavy oil upgrading by the removal of asphaltenes with nanoparticles, followed by catalytic thermal. In particular, the characteristics of nanoparticles of various metal oxides as adsorbents of asphaltenes extracted from oil sands have been evaluated [14,15]. Researchers have performed experiments evaluating the adsorption of asphaltenes on nanoparticles of Fe_3O_4, Al_2O_3, Co_3O_4, TiO_2, MgO, CaO, and NiO, obtaining equilibrium isotherms following a Langmuir-type behavior, in times less than 2 h. They also reported that the maximum adsorption capacity and adsorption affinity (Langmuir model parameters) were not always related [15]. Nassar [16] investigated the thermodynamic and kinetic aspects of the asphaltene adsorption onto alumina nanoparticles. Authors reported that asphaltene adsorption onto γ-Al_2O_3 nanoparticles was very fast, and equilibrium was achieved in less than 2 h. Pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data, with a better fitting to the pseudo-second-order model. Adsorption was highly dependent upon the initial concentration of asphaltenes, temperature, heptane/toluene ratio, and water content. The resultant isotherms were in good agreement with the Langmuir isotherm model. In a more recent study, Nassar et al. [17] used nanoparticles of iron oxide (Fe_3O_4) for the removal asphaltenes from toluene solutions by a batch adsorption technique followed by subsequent catalytic oxidation. According to the authors, adsorption was rapid and equilibrium was achieved within 10 min. The adsorption isotherms of the asphaltene samples tested were Langmuir type, suggesting monolayer coverage. It was found that the extent of adsorption increased with decrease in the molecular weight of the asphaltenes.

To the best of our knowledge, studies related to the thermodynamic equilibrium and kinetic of asphaltene adsorption onto hybrid nanomaterials such as nanoparticles of metal oxides supported on a nanoparticulated matrix of alumina have not been reported in the specialized literature. The aim of this study is to analyze the effect of temperature and NiO content on the asphaltene adsorption onto hybrid nanomaterials composed of nickel oxide nanoparticles supported on a nanoparticulated matrix of alumina. The alumina-supported nanomaterial was prepared by an incipient wetness technique widely used to prepare heterogeneous catalysts. Asphaltenes were isolated from a Colombian heavy crude oil.

2. Materials and methods

2.1. Materials

Asphaltenes were isolated from “The HOCHA” crude oil, which is a heavy oil (19.2 °API) produced from a reservoir located in the south of Colombia. Alumina nanoparticles (aluminum oxide) were supplied by Petroraza SAS. Reagents and solvents were purchased from Merck, Sigma Aldrich, and Fisher Scientific Co.

Alumina nanoparticles were dried at 120 °C and posteriorly impregnated with aqueous solutions of nickel nitrate $Ni(NO_3)_2$ at